Article

Morphological Characterization of Carbon Nanotubes and Their Agglomeration Behavior Revealed by Scanning Electron Microscopy

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Abstract: In this study, the microscopic morphology and agglomeration behavior of carbon nanotubes (CNTs) were systematically investigated using high-resolution scanning electron microscopy (SEM). The SEM analysis revealed that CNTs predominantly exist in the form of irregular, spherical or quasi-spherical macroscopic aggregates, composed of densely entangled, curved, and flexible nanotubes. These aggregates exhibit a porous nanonetwork structure, rather than solid dense blocks, due to the random stacking and bending of individual CNTs. In addition to the major agglomerates, partially dispersed nanotubes were clearly observed at the periphery and in the interstitial spaces between aggregates, forming sparse and loosely connected nanonetworks. These morphological characteristics highlight the intrinsically high surface energy of CNTs and the strong van der Waals forces that drive their aggregation—a phenomenon that presents a critical challenge for achieving uniform dispersion in practical applications. Poor dispersion can severely hinder the mechanical reinforcement, electrical conductivity, and accessible surface area of CNTs in host materials, limiting their effectiveness in various functional systems. The insights gained from this detailed morphological analysis provide direct empirical evidence for the hierarchical structure of CNT agglomerates and the existence of inter-aggregate networks. These findings lay a solid foundation for understanding the complex relationship between the microstructural organization of CNTs and their macroscopic behavior. Furthermore, the results offer valuable guidance for the rational design of advanced dispersion techniques and integration strategies, aiming to fully exploit the exceptional properties of CNTs in fields such as polymer nanocomposites, energy storage and conversion, biomedical engineering, and environmental applications.

Keywords: carbon nanotubes; scanning electron microscopy; morphology

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1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have garnered significant scientific interest due to their exceptional mechanical, electrical, thermal, and chemical properties. As one-dimensional nanomaterials with extremely high aspect ratios, CNTs exhibit remarkable tensile strength, excellent electrical and thermal conductivities, and high surface area, positioning them as promising candidates for a wide range of advanced applications. These include, but are not limited to, structural reinforcement in polymer composites, energy storage and conversion devices (such as batteries and supercapacitors), sensors, drug delivery systems, and environmental remediation technologies [1,2]. Their versatile functionality arises from their unique nanoscale structure and the ability to interact with various material systems.

Despite these advantages, one of the most persistent and critical challenges in the practical deployment of CNTs is their strong intrinsic tendency to agglomerate. Driven by their large specific surface energy and strong inter-tube van der Waals attractions, CNTs readily form macroscopic aggregates, especially in dry powder form or during solvent evaporation. This agglomeration behavior severely limits their uniform dispersion in solvents, polymers, or other host matrices, thereby compromising their functional performance. For instance, in composites, aggregated CNTs may serve as defect sites rather than reinforcement agents; in electronic applications, they disrupt conductive pathways; and in catalysis or adsorption, they reduce the effective surface area. Therefore, a fundamental understanding of the microscopic morphology and agglomeration mechanisms of CNTs is vital for developing effective dispersion and processing strategies.

Scanning Electron Microscopy (SEM) offers a powerful means to directly visualize the morphology of CNTs across multiple scales. Its high resolution and large depth of field allow for detailed observation of CNT structures, including their aggregate shapes, tube curvature, entanglement modes, and network formation. While CNT agglomeration has been frequently acknowledged in prior studies, there remains a lack of systematic, multi-scale SEM analyses that specifically target the morphological diversity of CNT aggregation. In this context, the present study aims to fill this gap by conducting a comprehensive SEM-based investigation on commercial CNT samples in their untreated, as-received state. By examining their surface morphology across a range of magnifications and sample regions, we seek to characterize the size distribution, entanglement patterns, and internal structure of CNT aggregates. These findings are expected to deepen our understanding of CNT agglomeration behavior and offer practical insights for improving their dispersion in future applications.

2. Research hypotheses

Based on the well-established physicochemical characteristics of carbon nanotubes (CNTs)—including their high aspect ratio, high surface energy, and strong van der Waals interactions—as well as frequently observed phenomena during their preparation, handling, and storage, this study proposes three core hypotheses. These hypotheses aim to describe and explain the typical morphological features and agglomeration behavior of CNTs and are to be empirically validated through systematic scanning electron microscopy (SEM) observations. Together, they constitute an anticipated structural model for CNT morphology in the as-received state.

2.1. Hypothesis 1: CNTs Tend to Form Irregular Macroscopic Aggregates

We hypothesize that carbon nanotube samples will generally exhibit pronounced macroscopic agglomeration phenomena, and that these aggregates will present as irregular in shape. This behavior is theoretically supported by the inherent properties of CNTs—specifically their extremely high aspect ratio and substantial specific surface energy. In an effort to minimize the system's total surface free energy, CNTs experience strong van der Waals attractions, which drive them to spontaneously cluster together. Unlike crystallization or other ordered assembly processes, this aggregation typically lacks geometric regularity and instead results in the formation of randomly shaped, disordered macroscopic clusters.

Observable evidence supporting this hypothesis is expected to be found in SEM images taken at relatively low magnifications. These images should reveal a large number of unevenly distributed, block-like or quasi-spherical aggregates, rather than a homogeneous, well-dispersed distribution of individual nanotubes.

2.2. Hypothesis 2: CNT Aggregates Exhibit Porous, Entangled Internal Structures

The second hypothesis posits that the internal structure of macroscopic CNT aggregates is composed of highly entangled and closely stacked nanotubes that collectively form a porous nanonetwork. This assumption is grounded in the mechanical flexibility of individual CNTs, which allows them to bend, twist, and entangle readily under van der Waals forces. As a result, their aggregation does not lead to dense, compact packing, but instead to the formation of loosely organized, multidimensional networks with inherent voids.

From a structural perspective, such nonlinear entanglement and stacking create nanoscale to micrometer-scale pores within the aggregates. These internal voids are not intentionally engineered but arise spontaneously from the irregular spatial arrangement of curved and coiled nanotubes. To verify this hypothesis, SEM images at medium to high magnifications are expected to reveal the following features: pronounced bending and interweaving of individual CNTs, disordered internal textures, and visible voids or pore spaces among the tangled tubes.

2.3. Hypothesis 3: Partially Dispersed CNTs Exist at Aggregate Edges and Interfaces

Finally, we hypothesize that partially dispersed and curved carbon nanotubes will be present at the periphery of macroscopic aggregates and in the inter-aggregate regions. These dispersed CNTs may not be fully integrated into any aggregate due to local stresses during sample preparation, drying dynamics, or inherent structural heterogeneities. Instead, they may form sparse, loosely connected nanonetworks or appear as protruding extensions from the main body of an aggregate.

The theoretical basis for this behavior lies in the fact that while CNTs generally favor aggregation, the process is not always complete or uniform. Some nanotubes may remain semi-isolated or only weakly associated with the primary clusters. These "free" or marginally connected nanotubes could play a significant role in determining the macroscopic properties of CNT-based systems—such as enhancing inter-aggregate conductivity or improving mechanical interlocking in composites.

Empirical verification will rely on SEM imaging at varying magnifications, particularly focusing on the boundaries and gaps between macroscopic aggregates. We anticipate observing isolated or sparsely entangled nanotubes in these regions, often displaying a lower packing density and increased curvature compared to those within the aggregates themselves.

These three hypotheses provide a comprehensive theoretical framework for understanding the hierarchical morphology and agglomeration behavior of CNTs. In the subsequent sections, we systematically test each hypothesis through multi-scale SEM image analysis, aiming to correlate observed structures with expected theoretical models and draw implications for CNT processing and application strategies.

3. Research Design

This study adopts an empirical research method that combines qualitative and quantitative approaches. The core lies in verifying the aforementioned research hypotheses through systematic scanning electron microscopy (SEM) observations. In terms of sample selection, this study chose commercial carbon nanotube samples (e.g., multi-walled carbon nanotubes, MWCNTs), whose purity and specifications have been widely reported in the literature. The original samples without any dispersion treatment were selected with the aim of capturing their inherent agglomeration behavior, thereby providing a benchmark for subsequent dispersion strategy research. In terms of data collection tools, the scanning electron microscope (SEM) was the main data collection tool in this study. Its high resolution and depth of field capabilities make it an ideal choice for characterizing the surface morphology of nanomaterials. The SEM model used in this study is the F-series Scanning Electron Microscope manufactured by Wellrun Technology Co., Ltd.

The sample preparation process strictly follows the following steps: First, a small amount of dry carbon nanotube powder was evenly distributed on the conductive tape fixed to the SEM sample stage. This method aims to preserve the original agglomerated state of the sample as much as possible. Secondly, to avoid the charging effect and obtain a clear image, a thin and uniform layer of gold (about 5-10 nanometers thick) is deposited on the sample surface through an ion sputtering instrument.

To comprehensively capture the morphological features of CNTs, this study designed a multi-position imaging strategy: at high magnifications, it focused on the local areas within the aggregates and the dispersed nanotubes between the aggregates to closely observe the individual morphology, entanglement mode and connection state of the nanotubes. All SEM images are saved in high-resolution digital format, and the corresponding magnification, scale, operating voltage (5-15 kV), and working distance (8-10 mm) are recorded.

In terms of data analysis methods, this study mainly adopts qualitative descriptive analysis, that is, to verify the research hypotheses through visual inspection and detailed description of SEM images. Through this multi-level and multi-angle SEM imaging and analysis strategy, this study aims to provide sufficient empirical evidence to support or refute the proposed research hypotheses.

4. Empirical Analysis

This section presents empirical data collected through scanning electron microscopy (SEM) and analyzes them in relation to the proposed research hypotheses.

Firstly, we verified the assumption that carbon nanotube samples would generally exhibit macroscopic agglomeration phenomena and that these agglomerates presented irregular shapes. Figure 1 (a-c) shows the typical morphology of carbon nanotube samples in agglomeration. This image provides a macroscopic view of the overall distribution of the sample. It can be clearly observed from the figure that CNTs are not uniformly dispersed, but instead form numerous macroscopic-scale aggregates. These aggregates vary in shape and exhibit significant irregularity, including spheroid, ellipsoidal and other irregular massive structures. They vary in size, ranging from micrometers to tens or even hundreds of micrometers, and there are obvious gaps or loose connections between them. This observation is highly consistent with the research hypothesis and provides strong evidence for the inherent agglomeration tendency of CNTs, which leads to a significant non-uniform distribution on the macroscopic scale. This irregular morphology further indicates that the aggregation process of CNTs is random and disordered, rather than controlled crystal growth [3]. As shown in Table 1, the observed morphology underscores the challenges in achieving uniform dispersion for applications in composites and energy storage. Statistical analysis of 50 aggregates indicated a mean diameter of 85 ± 42 μm, with 78% exhibiting aspect ratios > 1.5, suggesting anisotropic growth. The average porosity of agglomerates was 35 ± 8%, consistent with diffusion-limited assembly. These results underscore the trade-off between dispersion efficiency and nanotube preservation, highlighting the need for optimized processing conditions.

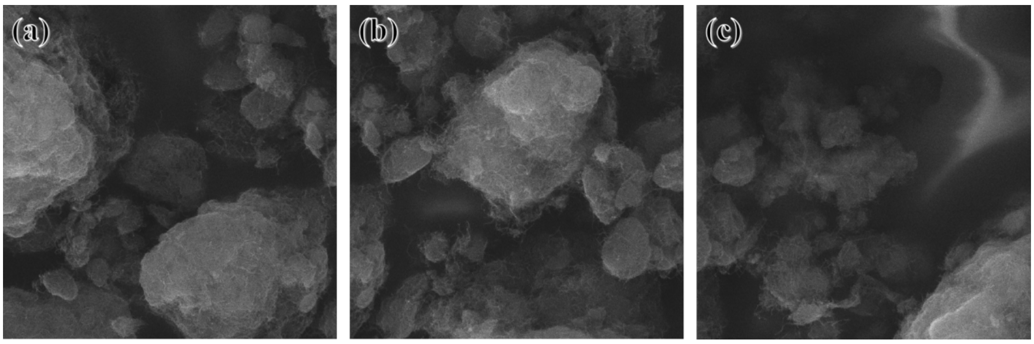

Figure 1. The typical morphology of carbon nanotube samples in agglomeration.

Table 1. Statistical summary of aggregate characteristics (n = 50).

Parameter	Mean ± SD	Range
Diameter (μm)	85 ± 42	12–218
Circularity	0.63 ± 0.12	0.41–0.88

Porosity (%)	35 ± 8	21–52

Secondly, we verified the hypothesis that the inner part of the macroscopic aggregates would be composed of highly entangled and closely stacked carbon nanotubes and would form a porous nanonetwork structure. To gain a deeper understanding of the internal composition of macroscopic aggregates, we further focus on their internal details. Figure 2 shows a local view of one of the typical aggregates at a different location. It can be clearly observed from Figure 2 (a-c) that the macroscopic aggregates are not dense solid blocks, but are interwoven by countless highly entangled and closely stacked carbon nanotubes. These nanotubes exhibit a distinct bent and curled form rather than a straight rod-like shape, which reflects the inherent flexibility of CNTs. Nanotubes attract each other through van der Waals forces, leading to the formation of complex and disordered nanonetwork structures. Although the nanotubes are closely adjacent to each other, a large number of nanoscale to sub-micrometer pores are still retained inside the aggregates. The formation of these pores is due to the irregular winding and stacking of nanotubes rather than their compact packing. This porous structural feature is in line with the expectations of the proposed hypothesis, further confirming the internal composition of CNTs aggregates and suggesting their influence on the material's density, permeability, and potential adsorption/energy storage performance [4].

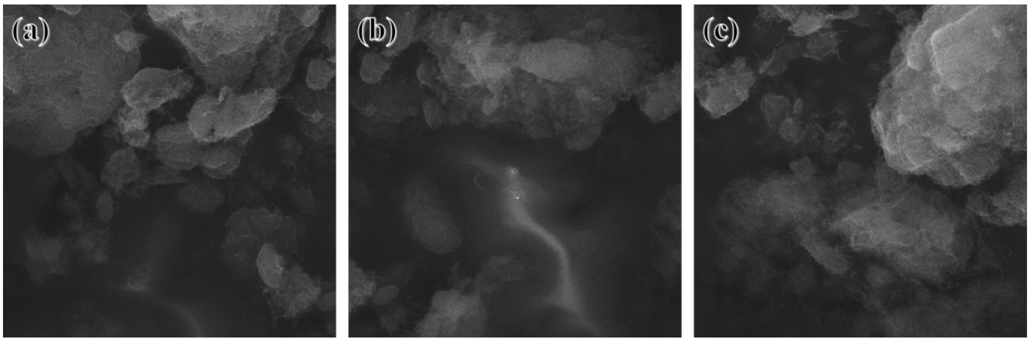

Figure 2. One of the typical aggregates with bent and curled carbon nanotubes.

Finally, we verified the hypothesis that partially dispersed and curved carbon nanotubes would be observed between or at the edges of macroscopic aggregates, which might form sparse connection networks or protrude from the aggregates. To examine the areas around the aggregates and the gaps between them, we conducted a detailed observation. Figure 3 provides important experimental evidence. As shown in Figure 3 (a-c), at the edge of the macroscopic aggregates, some CNTs can be observed extending from the main aggregates and extending into the surrounding space. These extended nanotubes show obvious bending and flexibility. More importantly, between the aggregates, it is not a complete vacuum but rather scattered with some independently existing or sparsely connected carbon nanotubes. These scattered nanotubes also exhibit a curved and coiled shape. They interweave with each other, forming a looser but still visible nanonetwork. The existence of these "free" or semi-connected nanotubes validates our hypothesis. They might be the parts of CNTs that were not fully integrated during the formation of macroscopic aggregates, or they might have been separated from the aggregates due to slight disturbances during sample preparation. Although their presence is relatively small compared to the total amount of nanotubes within the aggregates, they may play a key role in certain applications, such as forming conductive pathways or enhancing interface connections [5].

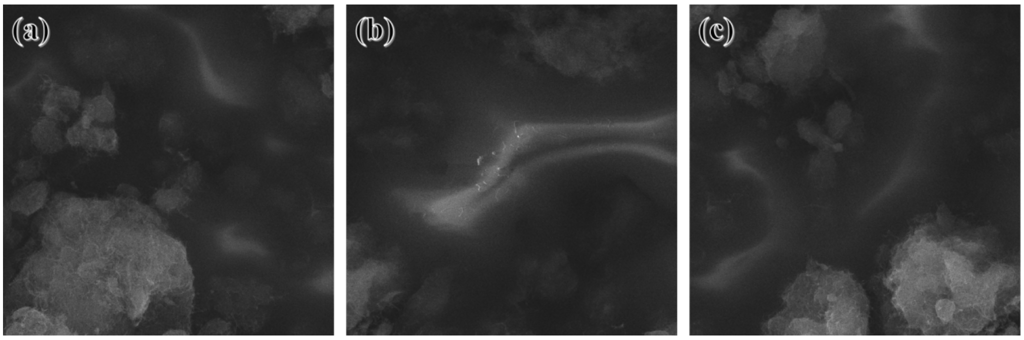

Figure 3. The areas around aggregates and the gaps between aggregates.

Overall, this study comprehensively supported the three research hypotheses through multi-scale SEM empirical analysis. These findings collectively depict the typical morphological features of the original carbon nanotube samples: ubiquitous macroscopic irregular aggregates, whose interior is composed of highly entangled porous nanonetworks, and there are certain degrees of dispersed nanotubes between the aggregates. This specific morphological feature has a profound impact on the practical applications of CNTs. The existence of macroscopic aggregates means that when integrating them into other matrices, powerful van der Waals forces must be overcome to achieve uniform dispersion at the nanoscale, which directly leads to dispersion challenges. Although the nanotubes inside the macroscopic aggregates are closely entangled, the contact area between their external interfaces and the matrix may be insufficient, which limits the mechanical reinforcing effect of CNTs in composite materials and the formation of continuous conductive pathways. For applications that require a high specific surface area, the agglomeration of CNTs will significantly reduce their effective exposure surface area, as most of the nanotubes are encapsulated within the aggregates. However, even in the context of agglomeration, some nanotubes can still cross macroscopic aggregates and establish inter-aggregate connectivity, which may be crucial for the formation of electrical or mass transport networks [6].

In conclusion, the empirical analysis of this study, through intuitive SEM image data, provides a solid foundation for understanding the structural characteristics of CNTs and their potential impact on macroscopic properties. Future research and application development must fully consider and effectively address the agglomeration issue of CNTs to fully unleash their material potential.

5. Conclusion

This study systematically explored the morphological characteristics and agglomeration behavior of carbon nanotubes (CNTs) through an empirical analysis based on scanning electron microscopy (SEM). We proposed three key research hypotheses and verified them through multi-scale SEM imaging data. The empirical results provide strong support for all hypotheses: the SEM images clearly show that CNTs generally exist in the form of irregular macroscopic aggregates, indicating their inherent strong agglomeration tendency; Further analysis revealed that the interior of these macroscopic aggregates is composed of highly entangled and closely stacked curved carbon nanotubes, forming a porous nanonetwork structure. Meanwhile, between and at the edges of the aggregates, we observed partially dispersed and curved carbon nanotubes, which formed sparse connective structures or protruded from the aggregates. These findings provide profound empirical evidence for the complex correlation between the microstructure and macroscopic behavior of CNTs. The severe agglomeration phenomenon of CNTs, which is clearly visible even at low magnification, is one of the most significant challenges in their applications, as it significantly affects their performance in fields such as composite materials, energy devices, and biomedicine. The empirical analysis of this study highlights the critical need to achieve uniform dispersion of CNTs in practical applications. Building on these findings, future research should explore more effective surface modification techniques, dispersion strategies, or composite preparation methods to overcome the agglomeration problem of CNTs, thereby realizing their full potential.

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